Synthesis, Characterization, and Evaluation of Cobalt (Co) and Iron (Fe)-Based Metal Organic Frameworks for Supercapacitor Studies

Synopsis in candidature for the degree of

Doctor of philosophy in physics

Submitted By

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1.1 Introduction

Presently, there is a considerable surge in the pursuit of energy storage systems characterized by elevated levels of both energy density and power density. Among these, supercapacitors have garnered significant attention as a particularly promising option. This is due to their inherent attributes, such as notably elevated power densities and extended operational lifespans that often surpass those observed in conventional batteries. [1]. Hence, the focal point of research endeavours in the realm of supercapacitors revolves around attaining augmented energy densities. The pivotal means to realize this objective lie in the innovation and creation of novel materials, underscoring their utmost significance in the pursuit of this aim. [2, 3].

Throughout the evolution of supercapacitor technology, porous materials have consistently emerged as a focal point of research interest. This is primarily attributed to their unique capability of facilitating rapid movement of both mass and electrons, consequently enhancing the efficiency of energy storage processes. [4]. Metal-organic frameworks (MOFs) are a novel category of hybrid materials, combining organic and inorganic materials. These structures possess customizable porous architectures and variable morphologies [5-6]. They have gained prominence as templates or precursors for generating metal oxides, porous carbons, and composite materials. These resultant materials tend to retain the porous characteristics of the original MOFs and exhibit improved electrochemical reactivity, particularly beneficial for applications in electrocatalysis and supercapacitors [7-8]. MOFs find utility in a wide array of domains including catalysis, sensing, and energy storage due to their adaptable nature. Their tailored porosity, stemming from deliberate selection of metal ions and organic ligands, makes them a versatile foundation for diverse applications [9-10].

1.2 Literature review

Over the past few decades, there has been a remarkable upsurge in enthusiasm and focus on metal-organic frameworks (MOFs). This particular class of materials is characterized by periodic structures formed by interconnected metal nodes and organic ligands, drawing substantial interest and attention from the scientific community [11-12].

The promising candidates emerging as potential supercapacitor electrode materials exhibit notable attributes such as a substantial surface area and the ability to modulate their size and irregular morphology. By manipulating the synthetic conditions, it becomes possible to exercise control over both the topological arrangement and the shape of these materials [13-14].

Constructing frameworks using MOFs offers a strategic approach to prevent the aggregation of metal nodes, leading to the development of downstream materials that exhibit exceptional characteristics as electrodes for supercapacitors [15-18]. Given that the organic components can undergo carbonization, this process substantially enhances the electrical conductivity while preserving the structural integrity of the configuration [16].

Nonetheless, the potential capacity during the assembly of a MOF or its derivative material remains constrained by the specific transition metal used. In order to push the boundaries and maximize the capabilities of MOF-derived materials as electrode candidates for supercapacitors, a more comprehensive exploration is required to delve into their intricacies and enhance their properties [19].

However, MOFs still face challenges such as the exposure of metals to the electrolyte, which can result in a low specific capacitance and poor stability of supercapacitors. Therefore, new strategies are needed to further develop MOFs for supercapacitor applications. One potential approach could be to optimize the synthesis conditions of MOFs to improve the morphology and composition of the materials to improve the overall performance, including energy density and cyclic longevity.

Hence, my intended development of action involves the synthesis of electrodes using Co-MOF, Fe-MOF, and bimetal MOF through one of the suitable chemical methodologies. This approach aligns with the goal of fabricating supercapacitor devices.

1.3 Aim

The overarching objective of this Ph.D. research is to meticulously investigate the synthesis, characterization, and electrochemical supercapacitor device fabrication of Co-MOF, Fe-MOF, and bimetal MOF.

1.4 Objectives:

The primary aim of this synopsis is to formulate and synthesize Co-MOF, Fe-MOF, and bimetal MOF structures, with the ultimate goal of fabricating supercapacitor devices exhibiting exceptional performance.

The proposed synopsis objective is as follows;

1.4.1. Synthesis of MOF Structures: Co-MOF, Fe-MOF, and bimetal MOF structures will be synthesized utilizing suitable chemical synthesis techniques.

1.4.2. Characterization of Nanostructured Electrodes: The structural and morphological attributes of the nanostructured electrodes will be thoroughly examined using a range of characterization

techniques including X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy.

1.4.3. Electrochemical Performance Evaluation: The electrochemical performance of the synthesized electrodes will be rigorously assessed under varied electrolyte solutions encompassing different molarities.

1.4.4. Rate Capability and Capacitance Retention Analysis: The ability of the electrodes to handle different charging and discharging rates will be examined, alongside an evaluation of their capacitance retention over time.

1.4.5. Fabrication of Supercapacitor Devices: The next step involves the fabrication of either symmetric or asymmetric supercapacitor devices, capitalizing on the insights gained from previous stages.

Through this systematic approach, the research aims to achieve high-performance supercapacitor devices based on the tailored properties of Co-MOF, Fe-MOF, and bimetal MOF structures.

1.5 Methodology:

Within the scope of this study, various chemical methods will be explored for the synthesis of Co-MOF, Fe-MOF, and bimetal MOF electrodes. Notable techniques encompass hydrothermal deposition (HD), the solvothermal method, and the slow diffusion technique. From these alternatives, an optimized approach will be selected for synthesizing electrodes based on M-MOFs, tailored for supercapacitor applications.

1.5.1 Hydrothermal Method:

The hydrothermal method offers a versatile means of synthesizing nanomaterials and metal oxides. This method carries significant advantages over other approaches. It can accommodate the production of nanomaterials that may not remain stable under high temperatures. Nanomaterials with elevated vapor pressures can be generated with minimal material loss. The hydrothermal synthesis process allows for meticulous control over the composition of the nanomaterials through liquid-phase or multiphase chemical reactions.

1.5.2. Solvothermal Method:

Solvothermal synthesis involves a chemical reaction transpiring in a solvent within a sealed container at temperatures surpassing the solvent's boiling point. This technique endows precise manipulation over particle size and shape distribution by adjusting reaction parameters.

The meticulous evaluation and selection of the most suitable synthesis method will be pivotal to the achievement of the research goals. This chosen approach will subsequently guide the fabrication of M-MOF electrode materials for enhanced supercapacitor performance.

Flexibility in the methodology is crucial to accommodate potential challenges and variations that may arise during the research process. Should the need arise, alternative synthesis methods will be considered and incorporated as deemed necessary. This adaptability ensures a comprehensive exploration of all viable avenues to achieve the desired results effectively.

1.6 Experimental section

The synthesized Co-MOF, Fe-MOF, and bimetal MOF electrodes will undergo comprehensive characterization using a range of analytical tools and techniques. These include X-ray diffraction (XRD), Raman spectroscopy, Fourier Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy (FE-SEM), High-Resolution Transmission Electron Microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray spectroscopy (EDS).

For the investigation of electrochemical properties and device fabrication, an electrochemical workstation will be employed. Various techniques will be employed, including cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), stability assessments, rate capability analysis, and impedance spectroscopy.

Ultimately, the culmination of this work will be presented as a thesis, submitted to the university as a requirement for the attainment of a Ph.D. degree. This comprehensive research endeavor is expected to contribute valuable insights to the field of supercapacitor electrode materials.

1.7 Work plan

The proposed work will be executed in a systematic manner, divided into the following phases:

Phase I (First Year):

During the initial year, an extensive literature survey will be conducted to establish a strong foundation for the research. Various synthesis methods will be explored and employed to create the distinct Co-MOF, Fe-MOF, and bimetal MOF electrodes.

Phase II (Second Year):

The second year will focus on assessing the electrochemical performance of the synthesized MOF electrodes. Comprehensive experimentation will be conducted in diverse electrolytes including KOH, H2SO4, NaOH, KCL, among others, to uncover a thorough understanding of their behavior.

Phase III (Third Year):

In the third year, the emphasis will shift towards exploring the practical applications of the developed Co-MOF, Fe-MOF, and bimetal MOF materials. This involves the fabrication of both symmetric and asymmetric supercapacitor devices, further highlighting the versatility and industrial potential of these materials.

Additionally, throughout the entire research timeline, regular communication will be established with high-impact scientific journals to disseminate the findings and contribute to the academic community.

This phased approach ensures a well-organized and comprehensive execution of the research project, leading to valuable insights and contributions in the realm of supercapacitor electrode materials.

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